AIAA 97-0599

Low Pressure Extrapolations for Soot Oxidation Rates

Robert Hiers

Sverdrup Technology, Inc., AEDC Group
Arnold Engineering Development Center
Arnold Air Force Base, Tennessee 37389

19980608 113

35th Aerospace Sciences Meeting and Exhibit

January 6-10, 1997 / Reno, NV

LOW PRESSURE EXTRAPOLATIONS FOR SOOT OXIDATION RATES*

*Robert Hiers***
Sverdrup Technology, Inc., AEDC Group
Arnold Engineering Development Center
Arnold Air Force Base, TN 37389-9013

Abstract

The carbon oxidation rates of Nagle and Strickland-Constable are routinely applied in the flame community to determine soot oxidation by molecular oxygen. These rates were experimentally determined at temperatures from 1000 to 2000°C (1273 to 2273 K) and at oxygen partial pressures from 0.1 to 0.6 atm and then curve fit. For typical laboratory flames, oxygen partial pressures may be significantly lower than 0.1 atm. Frequently, researchers will extrapolate the Nagle, Strickland-Constable (hereafter referred to as NSC) curve fits to these lower oxygen partial pressures to determine the molecular oxygen contribution to the overall soot oxidation rate. It is shown that the NSC curve fits exhibit nonphysical behavior at pressures below 0.05 atm (depending on the temperature). This behavior is revealed when the oxidation rates are transformed to collision efficiencies. At a fixed temperature, the oxidation rate drops faster than the collision rate as the pressure is reduced. At typical flame conditions, extrapolation of the NSC curve fits yields collision efficiencies that may be an order of magnitude too low.

Introduction

The carbon oxidation rates of Nagle and Strickland-Constable[1] are routinely applied in the flame community to determine soot oxidation by molecular oxygen. These rates were experimentally determined at temperatures from 1000 to 2000°C (1273 to 2273 K) and at oxygen partial pressures from 0.1 to 0.6 atm and then curve fit. For typical laboratory flames, oxygen partial pressures may be significantly lower than 0.1 atm. Frequently, research-

ers will extrapolate the Nagle and Strickland-Constable (hereafter referred to as NSC) curve fit to these lower oxygen partial pressures to determine the molecular oxygen contribution to the overall soot oxidation rate. For example, Lin, Sunderland, and Faeth[2] used the NSC rate expression to evaluate soot oxidation by molecular oxygen in 19-kPa (0.188 atm) acetylene/air diffusion flames. In their flames, the oxygen partial pressure ranged from 0.0004 to 0.004 atm on the flame axis. Puri, Santoro, and Smyth[3] also use the NSC expression to evaluate soot oxidation by O_2 in a variety of flames at oxygen partial pressures in the neighborhood of 0.02 atm.

Soot Oxidation Rates and Collision Efficiencies

Nagle and Strickland-Constable fit their oxidation rate data with the expression

$$
\begin{bmatrix}
\omega = \left(12.\left[\left(\dfrac{k_A P_{O_2}}{1+k_Z P_{O_2}}\right)\chi + (k_B P_{O_2})(1-\chi)\right]gm\ cm^{-2}sec^{-1}\right) \\
\text{where} \\
\chi = \left(1+\dfrac{k_T}{k_B P_{O_2}}\right)^{-1}, \\
k_A = 20\exp(-15100/T),\ gm\ cm^{-2}sec^{-1}atm^{-1}, \\
k_B = 0.00446\exp(-7640/T),\ gm\ cm^{-2}sec^{-1}atm^{-1}, \\
k_T = 1.51\times10^5\exp(-48800/T)gm\ cm^{-2}sec^{-1},\ \text{and} \\
k_Z = 2.13\exp(2060/T),\ atm^{-1}.
\end{bmatrix}
\quad (1)
$$

The specific soot oxidation rate (ω) is given as a function of temperature (T) in degrees Kelvin and oxygen partial pressure (P_{O_2}) in atmospheres. The NSC rate expression is plotted as a function of oxygen partial pressure and 1/temperature in Fig. 1. The expression is evaluated only over the exper-

Approved for public release; distribution unlimited.

imental range of these parameters, i.e. 1273 to 2273 K and 0.1 to 0.6 atm. Note that the oxidation rate is a monotonic increasing function of oxygen partial pressure.
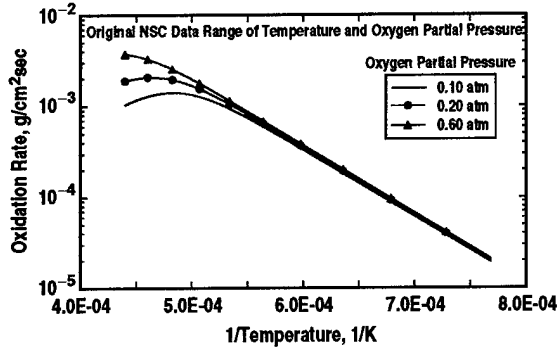

Fig. 1. NSC curve fit of oxidation rates.

The oxidation rate can also be expressed as a fraction of the total number of collisions with O_2; i.e.

$$\omega = Zf\tilde{m} \qquad (2)$$

or

$$f = \frac{\omega}{Z\tilde{m}} \qquad (3)$$

where Z is the collision frequency, Zf is the frequency of reactive collisions, f is termed the collision efficiency, and $\tilde{m}$ is the mass removed per reactive collision. The collision rate with O_2 is given by

$$Z = \frac{1}{4}n\bar{\upsilon}[O_2] = \frac{1}{4}\frac{P_\infty}{kT_\infty}\sqrt{\frac{8kT_\infty}{\pi m}}[O_2] \qquad (4)$$

where k is the Boltzmann constant, is the average molecular velocity, n is the number density, m is molecular mass, $[O_2]$ is the oxygen mole fraction, and P_∞ and T_∞ are the pressure and temperature of the ambient gas.

In Fig. 2, the results in Fig. 1 have been cast into the form of collision efficiency, assuming the reaction

$$2C(s) + O_2 \rightarrow 2CO. \qquad (5)$$

Each reactive collision with O_2 is assumed to remove two carbon atoms; therefore, $\tilde{m}$ is 24 gm-atoms for this reaction. The collision efficiency monotonically increases with decreasing pressure. In Fig. 3, the NSC oxidation rate expression is

again evaluated, but now extrapolations in both temperature and pressure are shown. The lower oxygen partial pressures in Fig. 3 are more typical of flame conditions. It is not obvious in Fig. 3 that anything is amiss. At a fixed temperature, the oxidation rate is a monotonic increasing function of oxygen partial pressure. In Fig. 4, the oxidation rates in Fig. 3 are recast as collision efficiencies. Over this pressure range, the collision efficiency is not a monotonically increasing function with
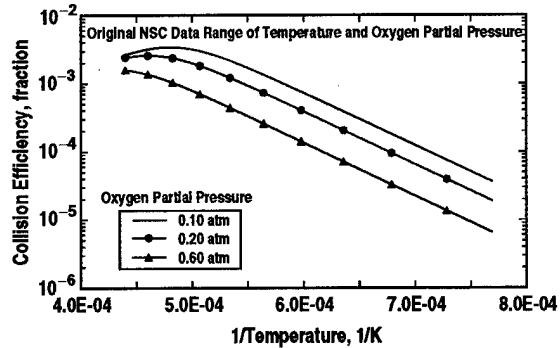

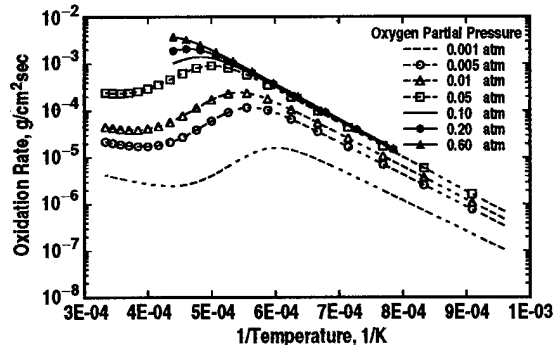Fig. 2. Curve fit of NSC collision efficiency.

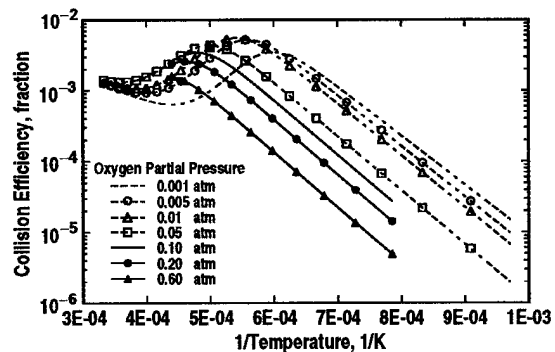Fig. 3. Extrapolations of NSC curve fit of oxidation rates.

Fig. 4. Extrapolations of NSC curve fit of collision efficiency versus 1/temperature.

decreasing pressure. As a convenience, Fig. 5 presents the same collision efficiencies as Fig. 4, plotted versus temperature rather than 1/temperature. Note that there is significant overlap of the curves in the 1700 to 2200 K temperature range - an important range for flames.
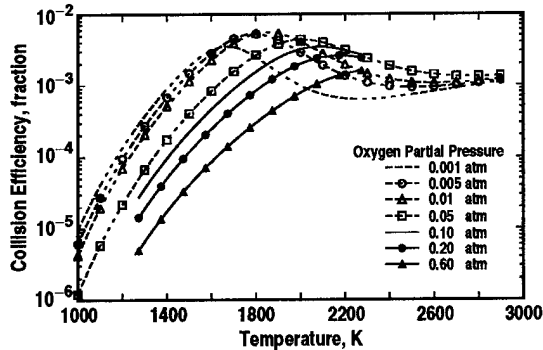

Fig. 5. Extrapolations of NSC curve fit of collision efficiency versus temperature.

To see the non-monotonic behavior more clearly, Fig. 6 presents the collision efficiency as a function of oxygen partial pressure for two temperatures–1250 and 2000 K. For 1250 K, the collision efficiency is a monotonically increasing function with decreasing pressure. This is the expected physical behavior. The pressure dependence of the oxidation rate is related to the occupation of active sites on the soot surface by other oxygen molecules (or atoms). At extremely low pressure, the collision efficiency is simply the ratio of the active surface area to the total surface area. This ratio is strictly a function of soot temperature. In order to fit their data, Nagle and Strickland-Constable used a modification of the surface reaction theory of Blyholder, Binford, and Eyring.[5] This theory states that the number of active sites on the surface is a function of temperature only, and is therefore independent of pressure. Active sites are occupied by oxygen molecules (or atoms) for a finite time, rendering these sites temporarily inactive. If the collision frequency is high enough, the molecules occupying the active sites will interfere with other molecules arriving at the surface. Therefore, increasing pressure causes an *apparent* decrease in the number of active sites on the soot surface. This is reflected as a decrease in the collision efficiency. The number of active sites on the surface is fixed by the temperature, but the availability of an active site is affected by the collision frequency. At high collision frequen-

cies, molecules collide with the soot surface faster than the occupied sites are cleared. This means that the collision efficiency must be a monotonically increasing function with decreasing pressure. As seen on Fig. 6, at 2000 K the collision efficiency computed from the NSC expression is not a monotonically increasing function with decreasing pressure. The efficiency has a maximum at about 0.02 atm and then decreases with further decrease in pressure. This decrease is not physical and violates the Blyholder-Binford-Eyring theory on which the NSC curve fit is based. It is caused simply by extrapolating the NSC expression beyond its range of validity.
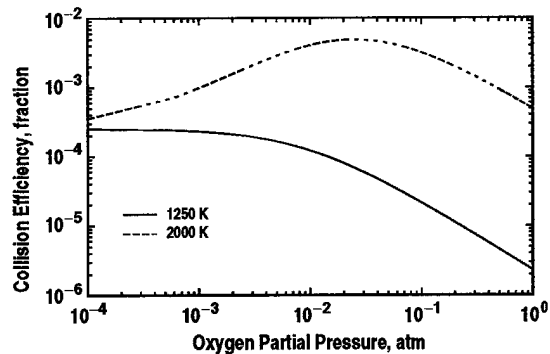

Fig. 6. Pressure dependence of NSC collision efficiency.

The collision efficiency is plotted as a function of pressure for various temperatures in Fig. 7. Note that at high temperature, the collision efficiency is nearly constant with pressure. This is due to the extremely short residence times in the active sites at high temperature. The pressure at which the collision efficiency is maximum is the lowest valid pressure for extrapolating the NSC rate expression. The locus of these minimum valid pressures is plot-
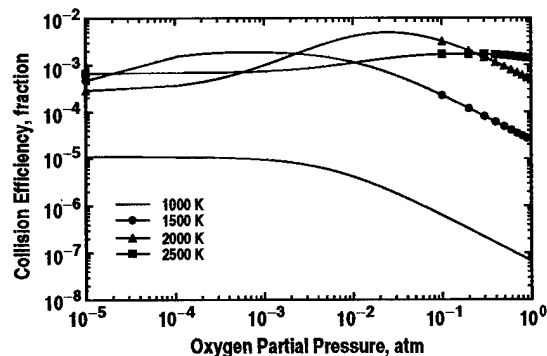

Fig. 7. Pressure dependence of collision efficiency for various temperatures.

ted as a function of temperature in Fig. 8. This figure gives a rapid estimate of the pressure at which the NSC rate expression may begin to be suspect. However, at temperatures greater than 2500 K the collision efficiency is relatively flat, so the error introduced at low pressure is small.
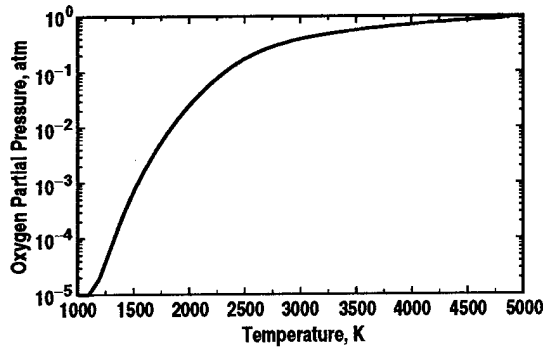

Fig. 8. Minimum valid pressure for NSC rate expression, derived from maximum collision efficiency.

There is another way to see the nonphysical behavior of the NSC rate expression without converting oxidation rates to collision efficiencies. Since the number of active sites on the surface is a function of temperature only, if pressure is reduced by some factor, the oxidation rate must reduce by the same factor or less. In other words, if the pressure is reduced a factor of two, the oxidation rate can, at most, decrease a factor of two. The same obviously holds true for increases in pressure. A doubling of pressure can produce, at most, a doubling in the oxidation rate. Therefore, a simple check is to normalize the pressure and the oxidation rate by their values at some given pressure. In Fig. 9, the normalized oxidation rate is plotted as a function of normalized pressure at a temperature of 2000 K. The pressure is normalized by 0.5 atm,
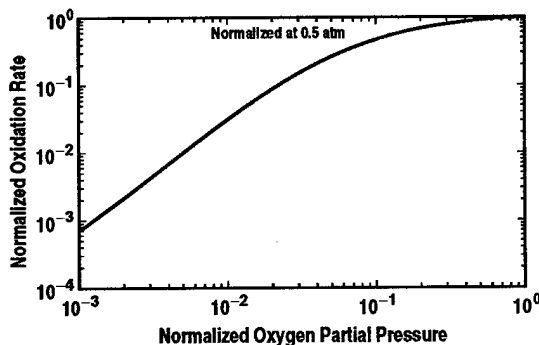

Fig. 9. Normalized oxidation rate versus normalized pressure at 2000 K.

and the oxidation rate is normalized by the oxidation rate at 0.5 atm. At a normalized pressure of 0.001, the normalized oxidation rate is 0.0007. This means that a reduction in pressure by a factor of 1000 produced a reduction in oxidation rate by a factor of 1500. This is clearly nonphysical and violates the Blyholder-Binholder-Eyring theory on which the NSC curve fit is based..

The oxidation rate must change by a factor equal to or less than the factor that the pressure is changed. If the oxidation rate changes by the same factor as the pressure, then

$$\frac{\omega}{P_{O_2}} = constant \qquad (6)$$

Taking the logarithmic derivative yields

$$\frac{d\omega}{\omega} = \frac{1}{\frac{dP_{O_2}}{P_{O_2}}} \qquad (7)$$

or

$$\frac{P_{O_2}}{\omega}\frac{\partial\omega}{\partial P_{O_2}} = 1.0 \qquad (8)$$

Since the oxidation rate can change by a smaller factor, the actual requirement can be defined as

$$G \equiv \frac{P_{O_2}}{\omega}\frac{\partial\omega}{\partial P_{O_2}} \leq 1.0 \qquad (9)$$

The indicated partial derivative can be evaluated analytically from Eq. (1). This quantity (G) is plotted as a function of pressure for various temperatures in Fig. 10. Whenever G is greater than one, the oxidation rate is changing by a greater factor than the pressure, and is therefore invalid. Comparing Figs. 8 and 10, it can be seen that G rises above unity at the same pressure at which the collision efficiency is maximum. Therefore, both methods of determining the minimum valid pressure for the NSC rate expression at a given temperature give the same results. The locus of pressures where G just rises above unity is plotted as a function of temperature in Fig. 11. This again gives an indication of the minimum pressure for which the NSC rate expression is valid. Note the similarity with Fig. 8. The two methods for determining the minimum valid pressure agree almost precisely.
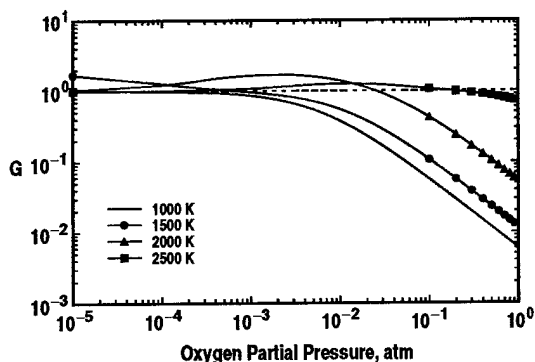
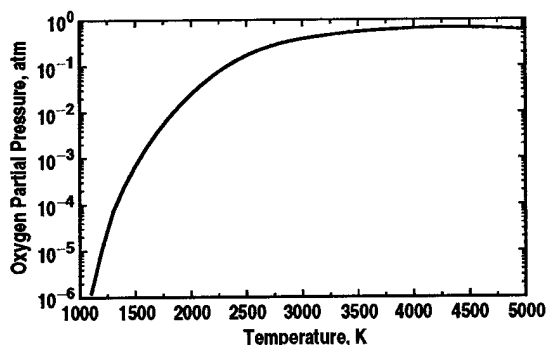Fig. 10. Pressure dependence of G for various temperatures.

Fig. 11. Minimum valid pressure for NSC rate expression, derived from G > 1.

Impact of Extrapolation on Oxidation Rates

To see the potential impact of extrapolation, consider a flame with an oxygen partial pressure of 0.001 atm and a temperature of 2000 K (approximating conditions of Lin, et al.). The NSC expression yields a collision efficiency of 8×10^{-4} at these conditions. However, the collision efficiency can be no less than that at the lowest pressure of the experimental NSC data (0.10 atm) which is about 3 $\times 10^{-3}$. Therefore, the NSC expression yields a collision efficiency that is at least a factor of 3-4 too low. Of course, the collision efficiency should actually continue to increase with decreasing pressure. If the collision efficiency at 2000 K is assumed to have the same pressure dependence as the efficiency at 1250 K, the NSC expression at 0.001 atm may be low by as much as a factor of 10 or more. This demonstrates that the nonphysical nature of the NSC rate expression can have a significant impact on soot oxidation rates at flame conditions.

Conclusions

The NSC rate expression is invalid when extrapolated to oxygen partial pressures typical of laboratory flames. The extrapolations exhibit non-physical behavior and produce collision efficiencies significantly lower than would be expected. The nonphysical behavior is revealed when the NSC oxidation rate expression is cast in the form of colli-sion efficiency. Oxidation rates obtained from the NSC oxidation rate expression at typical flame con-ditions may be an order of magnitude lower than expected on physical grounds. The surface reac-tion rate theory of Blyholder, Binford, and Eyring should not produce the non-physical behavior, since the theory assumes that the number of active sites is independent of pressure. Future work should include the fitting of the Nagle and Strick-land-Constable data using the unmodified Bly-holder, Binford, and Eyring theory to ascertain if the modifications introduced by Nagle and Strick-land Constable introduced an error. A new rate expression that does not exhibit this nonphysical behavior should be derived and compared with a variety of oxidation rate measurements that encompass a wide pressure range.

References

1. Nagle, J. and Strickland-Constable, R. F., "Oxidation of Carbon Between 1000-2000°C," Pro-ceedings of the 5th Conference on Carbon, Perga-mon Press, New York, pp. 154-164, 1961.

2. Lin, K. -C., Sunderland, P. B., and Faeth, G. M., "Soot Nucleation and Growth in Acetylene Air Laminar Coflowing Jet Diffusion Flames," Combus-tion and Flame, 104: 369-375 (1996).

3. Puri, R., Santoro, R. J., and Smyth, K. C., "The Oxidation of Soot and Carbon Monoxide in Hydrocarbon Diffusion Flames," Combustion and Flame, 97: 125-144 (1994).

4. Kennard, E. H., Kinetic Theory of Gases, McGraw-Hill, New York, pp. 176-180, 1938.

5. Blyholder, G., Binford, J. S. Jr., and Eyring, H., " A Kinetic Theory for the Oxidation of Carbon-ized Filaments," Journal of Physical Chemistry, 62, 263-267 (1958).

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE 6 Jan 1997	3. REPORT TYPE AND DATES COVERED Conference Report

4. TITLE AND SUBTITLE
Low Pressure Extrapolations for Soot Oxidation Rates
AIAA Paper No. 97-0599

5 FUNDING NUMBERS
F40600-95-C-0017

6. AUTHOR(S)
Robert Hiers

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Sverdrup Technology, Inc.
939 Ave C
Arnold AFB, TN 37389-9900

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AEDC/DOT
1099 Ave C
Arnold AFB, TN 37389-9013

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Presented at the 35th AIAA Aeropsace Sciences Meeting, Reno, NV January 6-10, 1997.

12a. DISTRIBUTION AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
The carbon oxidation rates of Nagle and Strickland-Constable are routinely applied in the flame community to determine soot oxidation by molecular oxygen. These rates were experimentally determined at temperatures from 1000 to 2000 C (1273 to 2273 K) and at oxygen partial pressures from 0.1 to 0.6 atm and then curve fit. For typical laboratory flames, oxygen partial pressures may be significantly lower than 0.1 atm. Frequently, researchers will extrapolate the Nagle, Strickland-Constable (hereafter referred to as NSC) curve fits to these lower oxygen partial pressuresto determine the molecular oxygen contribution to the overall soot oxidation rate. It si shown that the NSC curve fits exhibitt nonphysical behavior at pressures 0.05 atm (depending on the temperature). This behavior is revealed when the oxidation rates are transformed to collision efficiencies. At at fixed temperature, the oxidation rate drops faster than the collsion rate as the pressure is reduced. At typical flame conditions, extrapolation of the NSC curve fits yields collision efficiencies that may be an order of magnitude too low.

14. SUBJECT TERMS
soot, oxidation, particulates, oxidation rate

15. NUMBER OF PAGES
6

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL